NEW SETS OF EXPERIMENTAL WAVENUMBER VALUES FOR TRIPLET-TRIPLET ROVIBRONIC TRANSITIONS OF H_2 AND D_2

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New sets of experimental wavenumber values for triplet-triplet rovibronic transitions of H_2 and D_2 for visible part of spectrum ($400 \div 700$ nm) have been obtained. The digital intensity registration providing a linear response of the detector gave us the opportunity of digital deconvolution of the recorded line profiles. For line centers that made it possible to reach an accuracy limited only by selfconsistency of various wavenumber standards. New set of data was obtained with accuracy $0.006 \div 0.05$ cm^{-1}.

At present almost all available experimental data on rovibronic line wavenumbers of H_2 and D_2 molecules were obtained from emission spectra by photographic recording. Our recent studies revealed that these data have significant differences with values predicted by Rydberg-Ritz combination principle as well as with fragmentary experimental data obtained by laser induced fluorescence and with our own emission spectroscopy data obtained with photoelectric recording by matrix detectors (2008 Russ.J.Phys.Chem.B, 2 16-31; J. Phys. B: At.Mol.Opt.Phys. 41 105103). The minority of the differences is caused by misprints and erroneous line assignments; they may amount to several wavenumbers. But vast majority of them amount $0.01 \div 0.1$ cm^{-1} and show random spread around "synthesized" values, calculated as differences of optimal energy level values. We suppose that they appear due to shifts of film blackening maxima for blended lines, finite precision of reading from photo plates, and round-up errors in calculating the wavenumbers from measured wavelengths in air.

To refine our knowledge of rovibronic term structure for isotopomers of the simplest

neutral molecule we launched systematic measurements of the rovibronic line wavenumbers in visible part of spectrum ($400 \div 700$ nm). The 2.65 m Ebert-Fastie spectrograph was equipped with additional camera lens and computer-controlled CMOS matrix (22.2x14.8 mm, 1728x1152 pixels) providing the reverse linear dispersion about 10^{-3} nm/pixel. We used various light sources: glow discharge in $Hg + Ar$ (for determination of instrumental broadening from the superfine structure of 404.6 nm and 546.1 nm mercury lines: Gaussian shape with FWHM = 0.183(9) and 0.143(9) cm^{-1}, much smaller than Doppler broadening of H_2, D_2 lines for our gas temperatures < 1500 K), a capillary-arc discharges filled with the mixture $D_2 + H_2 + Ne$ (for studies of the precision of spectrometer calibration) and with pure H_2 or D_2 (for final wavenumber measurements).

We calibrated our spectrometer with available wavelengths in vacuum to avoid precise determination of refractive index of air in our conditions. The wavenumber values of finite number of strong unblended lines of H_2 (G.H.Dieke 1972), D_2 (H.M.Crosswhite 1985) and Ne (www.nist.gov) were used as standards. The dependence of line wavenumber on the coordinate (in pixels) is monotonic and close to linear. The calibration curve of the spectrometer was obtained by the least-squares fitting by a second-degree polynomial (a linear approximation was insufficient, while a third-degree polynomial superfluous).

The digital intensity registration providing a linear response of the detector gave us the opportunity of digital deconvolution of the recorded line profiles. For strong unblended lines profiles were close to the Gaussian shape except for insignificant far wings. Therefore, we approximated all parts of the spectrum by Gaussian multipeak fitting with fixed half-width and adjustable intensity and wavelength values for peak maxima. Thus we obtained wavenumbers of rovibronic radiative transitions for triplet-triplet band systems.

The contribution contains the details of experimental technique and results.